

Plutonium Pyrochemical Salts Oxidation and Distillation Processing: Residue Stabilization and Fundamental Studies

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Vanadium pentoxide, V_2O_5 , has been proposed as an oxidant for the stabilization of pyrochemical salt residues from plutonium pyrochemical processes at the Rocky Flats Environmental Test Site because of its large reduction potential and its ability to react via normal solid-state reactions (i.e. no solvents are required). The pyrochemical salt residues contain plutonium in reactive forms and lower oxidation states (the most common forms being Pu^0 , $PuOCl$, and $PuCl_3$) along with several alkali or alkaline earth chlorides. These residues present an environmental hazard because compounds with plutonium in oxidation states less than IV are unstable with respect to air-oxidation, and deleterious reactions with water and other small molecules can occur. The ideal stabilization process would result in the concentration of a Pu-rich heel containing primarily PuO_2 , an ideal form for long-term storage or disposition, and a Pu-poor salt phase, that may be disposed of as low-level waste.

When V_2O_5 was used to oxidize actual process residues, results were highly variable. There are no published reports of the chemical oxidation of plutonium with vanadium pentoxide in molten salts; in addition, the solid-state reaction chemistry of plutonium with vanadium oxides has not been well studied. This work is the first systematic study of the chemical oxidation of plutonium with vanadium pentoxide.

The reaction chemistry of $PuCl_3$, Pu^0 and $PuOCl$ with V_2O_5 in the presence and absence of a NaCl/KCl salt matrix and under a variety of conditions will be presented. Our studies are intended to address three distinct questions: (1) Is V_2O_5 a suitable oxidant to convert Pu^0 and $Pu(III)$ to $Pu(IV)$? (2) What is the identity of the reaction products, and are they volatile? And (3) what are the optimal process conditions for these reactions?

Results of the $PuCl_3$ reactions indicate an equal to or greater than 1:1 $PuCl_3$: V_2O_5 ratio is needed for complete oxidation of $PuCl_3$. Products from 3:2 $PuCl_3$: V_2O_5 reactions clearly contain unreacted $PuCl_3$. Increasing the amount of V_2O_5 from one to two equivalents increases the contribution of side reactions, including reactions of V_2O_5 with the process equipment and/or salt matrix, and produces undesirable non-volatile ternary and quaternary vanadium compounds.

The Pu^0 oxidations are more complex than the $PuCl_3$ oxidations. More unreacted Pu^0 remains in a reaction using more equivalents of V_2O_5 than a reaction using a smaller amount of V_2O_5 . The lack of predictability of these reactions may be due to several factors and will be discussed. Complete oxidation of Pu^0 to $Pu(IV)$ in the presence of the salt matrix does not occur with up to six equivalents of V_2O_5 . Chlorine is detected in the off-gas of the Pu^0 oxidations, indicating the salt matrix participates in the reaction(s) that hinder oxidation. The interference of the salt matrix is further confirmed by the fact that conversion of Pu^0 to $Pu(IV)$ occurs almost instantaneously in the absence of the salt matrix.

Reactions involving $PuOCl$ are similar to the $PuCl_3$ oxidations. Greater than a 1:1 $PuOCl$: V_2O_5 ratio is required to achieve adequate conversion of the plutonium phase to PuO_2 .

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